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THE INVERSION OF SPECTRAL DATA OF AlCl AND SiS $X^1\Sigma^+$ *

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Analysis of all available data of published pure rotational and vibration-rotational spectra of $Al^{35}Cl$, $Al^{37}Cl$, and SiS in various isotopic variants yielded values of coefficients of radial functions for the potential energy and other molecular properties for the electronic ground states $X^1\Sigma^+$; only ten independently fitted parameters sufficed to reproduce satisfactorily and with physical meaning the frequencies and wavenumbers of about 890 distinct pure rotational and vibration–rotational transitions of AlCl, but ten parameters were fitted to 3025 transitions of SiS with two constrained parameters. Effectively independent of nuclear mass, the equilibrium internuclear separation of AlCl $R_e/10^{-10}\mathrm{m} = 2.1301429 \pm 0.0000019$, and the maximum range of validity of the radial functions is $1.90 \leq R/10^{-10}\mathrm{m} \leq 2.48$, whereas for SiS $R_e/10^{-10}\mathrm{m} = 1.9292731 \pm 0.0000016$ and the maximum range of radial functions is $1.72 \leq R/10^{-10}\mathrm{m} \leq 2.25$. Comparisons with previously published results of both AlCl and SiS are made.

1. Introduction

During the past century the range of gaseous molecular species amenable to detection by means of their vibration–rotational and rovibronic spectra has greatly expanded. Concurrently, the resolving power of spectral instruments has become improved such that for even the most massive diatomic species having several isotopic variants the rotational and, in many cases, even the hyperfine structure can be resolved; to evaluate the parameters that describe the molecular structure and properties we require analysis of this fine and hyperfine structure. During the past quarter century since the appearance of the monograph by Kovács [1], the formulae therein and in succeeding papers have greatly facilitated the analysis of the complicated rotational structure of molecules with net electronic spin and orbital angular momentum in terms of conventional spectral parameters; this treatment is applicable to both the frequencies and the intensities of distinct lines to which one can assign the vibrational and rotational quantum numbers of the combining states.

For molecules belonging to the simplest class $^1\Sigma$, the formulae to represent wavenumbers of vibration–rotational lines in terms of spectral parameters, such as

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* Dedicated to Professor István Kovács on his eightieth birthday

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ω_e, B_e, D_e etc., are almost trivial. We sought to extend analysis of the spectra of diatomic molecules beyond spectral parameters to not only molecular parameters but even to coefficients of pertinent radial functions, the functions of internuclear distance R. Provided that spectral data of isotopic variants of each nuclide are available, we endeavour to eliminate all dependence on nuclear mass so as to evaluate molecular parameters; these parameters reflect directly the electronic structure of the molecule in a particular electronic state. Although such radial functions are meaningful formally within the approximation of separate treatment of nuclear and electronic motions, according to the treatment of Born and Oppenheimer and subsequent developments [2], if for electronic states — and the vibration–rotational states associated therewith — the energies differ sufficiently from those of other electronic states, the observable deviations from conformity to this approximation can still be encompassed in radial functions auxiliary to the internuclear potential energy that is the dominant effect. Such radial functions result from classical ideas of molecular structure, in particular the idea of two atoms connected by a chemical bond. Of effects [3] nominally of three kinds to take into account the internal structure of each 'atom', for adiabatic effects the internuclear potential energy depends on not only the separation but also the relative momenta of the individual nuclei; for nonadiabatic rotational and vibrational effects the electrons follow imperfectly one or other nucleus in its rotational and vibrational motions, respectively. A further effect whereby vibration–rotational energies fail to conform to properties of mass scaling involves not the mass of an individual nucleus, nor the reduced mass of the molecule, but the spatially finite and isotopically variable distribution of charge of either nucleus [4]. Application of the latter effect requires knowledge of the nuclear volume and its isotopic dependence, which is much less common and precise than for atomic mass [5], and so far such effects are distinguished for only relatively massive nuclei. The relative importance of these effects for a particular diatomic molecular species remains to be assessed during the analysis of the available spectra.

We have devised an algorithm, based on fully quantum-mechanical principles within the Born–Oppenheimer approximation but eventually transcending to some extent this limit, according to which we invert vibration-rotational spectral data of diatomic molecules to yield the fundamental radial functions of potential energy and auxiliary effects. In the present work we analysed spectral data of AlCl recently reported [6]. In this case nuclides of both types are moderately massive, but neither is sufficiently large for the effects of nuclear volume likely to be detectable. Although this molecular species possesses isotopic variants of Cl, because ^{35}Cl and ^{37}Cl exist in comparable proportions, Al consists of only the stable nuclide ^{27}Al. For comparison with the results of our spectral analysis of AlCl we selected SiS, which we previously analysed [7] before completing the theory that enables the treatment of all extra-mechanical effects [8]. For SiS there exist not only abundant pure rotational and vibration-rotational transitions of several isotopic variants, because of stable nuclides ^{28}Si, ^{29}Si, ^{30}Si, ^{32}S, ^{33}S and ^{34}S that exist in natural abundance to a practical extent, but also data from the Stark [9] and Zeeman effects [10] in various vibrational states. With our refined theoretical basis we employ this information to achieve a profound analysis so to acquire insight into the relative importance of of various factors that affect the wavenumbers of spectral transitions. In what follows we outline the basic theory and then apply it to deduce the maximum information about the intramolecular dynamics of these formally isoelectronic diatomic molecular species AlCl and SiS.

2. Theoretical basis of spectral analysis

As the basis of a quantitative treatment we adopt an effective Hamiltonian for nuclear motion of the form [11]

$$\mathcal{H}_{eff} = \hat{P}[1+\beta(R)]\hat{P}/2\mu + V(R) + V'(R) + hcB_e[1+\alpha(R)]J(J+1)R_e^2/R^2. \quad (1)$$

R is the internuclear separation and R_e its value at the minimum of potential energy, μ is the reduced mass, $B_e \equiv h/(8\pi^2 c\mu R_e^2)$ is the equilibrium rotational parameter, $\hat{P}$ is the operator for linear momentum of the nuclei, and $V'(R)$, $\alpha(R)$ and $\beta(R)$ represent adiabatic and nonadiabatic effects to be explained subsequently. To apply this Hamiltonian we transform to the reduced displacement variable

$$z \equiv 2(R-R_e)/(R+R_e) \quad (2)$$

that possesses the property of remaining finite throughout the range of molecular existence: for $0 \leq R < \infty$, $-2 \leq z < 2$ [12, 13]. With units of wavenumber henceforth assumed for appropriate quantities in conformity with spectral conventions and with SI units for all quantities in accordance with recommendations of IUPAP [14], the potential energy $V(R)$ formally independent of nuclear mass we represent in the form [12]

$$V(z) = c_0 z^2 (1 + \sum_{j=1} c_j z^j). \quad (3)$$

For an assumed diatomic molecule AB having nuclei of unequal atomic numbers, the further functions in Eq. (1) dependent on individual nuclear masses M_a and M_b we represent by means of separate expansions for each nucleus of types A and B; for nonadiabatic vibrational effects [11] whereby electrons follow imperfectly the nuclei during the oscillations of the latter with respect to the centre of mass, we have

$$\beta(R) \rightarrow \beta^a(R) + \beta^b(R) \rightarrow m_e(\sum_{j=0} s_j^a z^j/M_a + \sum_{j=0} s_j^b z^j/M_b) \quad (4)$$

for the nonadiabatic rotational effects whereby the electrons follow imperfectly the nuclei during the rotations of the latter about the centre of mass,

$$\alpha(R) \rightarrow \alpha^a(R) + \alpha^b(R) \rightarrow m_e(\sum_{j=0} t_j^a z^j/M_a + \sum_{j=0} t_j^b z^j/M_b) \quad (5)$$

and for the contribution to the internuclear potential energy dependent on nuclear mass, i.e. generally the adiabatic effects whereby the potential energy depends not only on the distance between the nuclei but also (slightly) on their relative momenta, hence on their individual masses,

$$V'(R) \rightarrow V^a(R) + V^b(R) \rightarrow m_e\Big(\sum_{j=1} u_j^a z^j/M_a + \sum_{j=1} u_j^b z^j/M_b\Big). \qquad (6)$$

As nuclear masses are known generally much less accurately than atomic masses and as the discrepancies between these masses have immaterial effects on the ultimate parameters and their interpretation, we henceforth employ atomic masses [5]. The discrete molecular energies within a particular electronic state, or vibration–rotational terms, we express in the form [11]

$$\tilde{E}_{vJ} = \sum_{k=0}\sum_{l=0}(Y_{kl} + Z_{kl}^{r,a} + Z_{kl}^{r,b} + Z_{kl}^{v,a} + Z_{kl}^{v,b})(v + 1/2)^k(J^2 + J)^l. \qquad (7)$$

Here the term coefficients Y_{kl} depend, in a nonlinear manner, on only the equilibrium force coefficient k_e (through $U_{1,0}$, defined below), the equilibrium nuclear separation R_e (through $U_{0,1}$, with $c_0 \equiv U_{1,0}^2/4U_{0,1}$), the reduced mass μ and the coefficients c_j in the radial function, Eq. (3), for potential energy. To take into account vibration–rotational ramifications of adiabatic and nonadiabatic effects, the term coefficients Z_{kl}^v of separately each nucleus a or b depend on the preceding parameters plus coefficients s_j^a, u_j^a and M_a or s_j^b, u_j^b and M_b, respectively, whereas for the additional rotational consequences of these effects the coefficients Z_{kl}^r of nucleus a or b depend on parameters in the first group plus s_j^a, t_j^a and M_a or s_j^b, t_j^b and M_b, respectively. In Eq. (7) the explicit dependencies of E_{vJ}, Y_{kl} and various Z_{kl} on the isotopic variant are suppressed. To treat adiabatic and nonadiabatic effects, which imply the coupling of electronic and nuclear motions, by means of radial functions of R, which imply the separate treatment of these motions, may appear incongruous; for the electronic ground state and in particular for its vibration–rotational states far from the dissociation limit, the formal interactions with energetically distant, electronically excited states may, however, be sufficiently weak that they can be considered to represent small and homogeneous perturbations [8].

Our fitting programme Radiatom [11] yields not only primarily the coefficients of radial functions defined according to the above relations, but also secondarily parameters U_{kl} and $\Delta_{kl}^{a,b}$ in the empirical relation [15]

$$\tilde{E}_{vJ} = \sum_{k=0}\sum_{l=0} U_{kl}\mu^{-(\frac{1}{2}k+l)}(v + 1/2)^k(J^2 + J)^l[1 + m_e(\Delta_{kl}^a/M_a + \Delta_{kl}^b/M_b)], \qquad (8)$$

in which coefficients U_{kl} are related to only parameters R_e and coefficients c_j, $j \geq 0$, whereas coefficients $\Delta_{kl}^{a,b}$ are related to coefficients in all radial functions 3 – 6; coefficients U_{kl} and $\Delta_{kl}^{a,b}$ are formally independent of mass. Two coefficients U_{kl}

have special significance: related to R_e, $U_{0,1} \equiv h(8\pi^2 cR_e^2)^{-1}$, and related to k_e, $U_{1,0} \equiv k_e^{1/2}(2\pi c)^{-1}$, both formally independent of nuclear mass.

Even though these adiabatic and nonadiabatic effects are mathematical artifacts, for the reason just stated, we associate experimental information with specifically the nonadiabatic rotational effects. The rotation of an otherwise non-magnetic diatomic molecule induces a small magnetic dipolar moment [16]; interaction of this molecular moment with an externally applied magnetic field produces splitting of spectral lines according to the Zeeman effect. The rotational g factor, or g_J, that is proportional to the magnetogyric ratio, the quotient of the induced rotational magnetic dipolar moment and the rotational angular momentum, is a measure of the extent of the splitting, according to the quantum number M_J, of the energy of a particular vibration–rotational state (for $J > 0$). The factor g_J is thus an expectation value $< vJ|\alpha(R)|vJ >$ or $< vJ|g_J(R)|vJ >$ of a particular state denoted by vibrational quantum number v and rotational quantum number J. For a net electrically neutral diatomic molecule of relative electric polarity $^{+}AB^{-}$, there arise two contributions to the g factor: g_J^{na} attributed to interaction between electronic and nuclear motions, and the other due to a rotating electric dipolar moment μ_e (at the equilibrium internuclear distance R_e) [17]:

$$g_J = g_J^{na} + m_p(M_a^{-1} - M_b^{-1})\mu_e/(eR_e), \tag{9}$$

in which m_p is the mass of the proton and e its electric charge. The equations, adapted from [18], for partition of the g factor into contributions of the separate atomic centres thus become

$$t_0^a = \mu[g_J/m_p + 2\mu_e/(eR_eM_b)], \tag{10}$$

$$t_0^b = \mu[g_J/m_p - 2\mu_e/(eR_eM_a)]. \tag{11}$$

The effective Hamiltonian contains radial functions of three kinds beyond mechanical effects embodied in the potential energy $V(z)$ [11], namely functions for adiabatic, nonadiabatic rotational and nonadiabatic vibrational effects of atomic centres of each type; in practice information of at most two kinds can be generally deduced from spectra recorded for samples without externally applied fields, namely the dependence on individual atomic (or nuclear) masses and the extra rotational effects. Measurements of the rotational g factor in varied vibration–rotational states according to the Zeeman effect provide additional information that enables one in principle to evaluate separately the nonadiabatic rotational effects [11]. For few molecules, although among them SiS [9], has the vibrational dependence of g_J been measured, but for AlCl neither g_J nor μ_e is precisely evaluated from experiment.

3. Application of theory to spectra of AlCl and SiS

The set of wavenumber data of SiS that we used in our analysis is described in our previous account [7]. For AlCl we fitted 2299 transitions in total: 70 were pure rotational transitions of $^{27}Al^{35}Cl$ up to $v = 8$, 47 were pure rotational transitions of $^{27}Al^{37}Cl$ up to $v = 5$, 1473 were vibrational-rotational transitions of $^{27}Al^{35}Cl$ in the progression $\Delta v = 1$ up to $v' = 8$, and 708 were vibration–rotational transitions of $^{27}Al^{37}Cl$ in the progression $\Delta v = 1$ up to $v' = 4$; the sources of these data are specified elsewhere [6]. To set the weighting factors of each line we fitted separately each vibration–rotational band to the band parameters ν_0, $B_{v'}$, $B_{v''}$, $D_{v'}$ and $D_{v''}$ in sets that ensured adequate fits of the data; obvious outliers (generally overlapping or blended lines) were assigned appropriately increased uncertainties to suppress their influence on the results. Because resulting standard deviations of fits of individual bands lie within a relatively narrow range, we selected a median value 0.23 m^{-1} from this range as the uncertainty of each vibration–rotational line not obviously subject to displacement or distortion. The uncertainties of pure rotational transitions reflected values specified by the original authors. In the fit of all data the weight of each line was the reciprocal square of its uncertainty of measurement. In calculations of R_e and k_e, we took account of uncertainties of pertinent physical constants [19]; each specified uncertainty signifies a single standard error.

In our previous analysis of all available pure rotational and vibration–rotational spectra of SiS [7], we fitted 3025 transitions with only twelve independently adjustable parameters, namely $U_{1,0}$, $U_{0,1}$, $c_1 - c_6$ and four parameters h_1^{Si}, h_2^{Si}, h_1^{S} and h_2^{S} that correspond to u_1^{Si}, u_2^{Si}, u_1^{S} and u_2^{S} in the same order. According to a refined procedure based on our advanced theory [11], we have since been able not only to relate the coefficients s_j, t_j and u_j to particular nonadiabatic vibrational and rotational, and adiabatic effects, respectively, but also to incorporate pertinent experimental information other than merely measured frequencies of pertinent transitions. In particular, we employ the rotational g factor and the electric dipolar moment according to Eqs (10) and (11) to yield precise values of $t_0^{a,b}$; to evaluate these by means of fitting is generally difficult. When by this means we deduced the values of t_0^{Si} and t_0^{S} listed in Table I, constrained thus these values in the fit of the same 3025 transitions, and proceeded to let the values of u_1^{Si}, u_2^{Si}, u_1^{S} and u_2^{S} be freely adjusted during the fit, we found that the derived values of both u_1^{Si} and u_1^{S} assumed magnitudes small relative to those of h_1^{Si} and h_1^{S} previously and even smaller than their standard errors. Because $u_1^{a,b}$ reflect entirely adiabatic effects [11], clearly these results imply that adiabatic effects are negligible for SiS, at least for the coefficient of z^1 in the relevant radial functions in Eq. (6). By comparison of the algebraic equations relating the former empirical parameters h_j [20] to the physically more meaningful parameters s_j and u_j [11] of the vibration–rotational extra-mechanical effects, one sees that h_2 is related to u_2 and to s_0. If adiabatic effects are negligible for coefficients of z^1 then one may reasonably assume that they are likely also negligible for coefficients u_2 of z^2; instead we sought to evaluate the coefficients s_0 that occur in the same relations primarily for $Z_{1,0}^{v,a}$ and $Z_{1,0}^{v,b}$ and secondarily for other coefficients $Z_{kl}^{v,a}$ and $Z_{kl}^{v,b}$ of higher order. Thus we obtained the parameters in Table I in the column for SiS. The normalised standard deviation of the fit was 0.71 and the F-value (that takes into account both the sum of squares of residuals and the number of fitted parameters) was 1.2×10^{15}. The maximum range of validity of these radial functions of SiS is $1.72 \leq R/10^{-10}\mathrm{m} \leq 2.25$.

Because spectra of AlCl are available for only molecules containing nuclides ^{27}Al and ^{35}Cl and ^{37}Cl [6], one cannot evaluate directly any parameters s_j^{Al}, t_j^{Al} and u_j^{Al}. Moreover because neither the rotational g factor nor even the electric dipolar moment is (precisely) available from experiment, we could not fix t_0^{Al} indirectly by means of Eq. (10). Therefore, we attempted to fit only s_j^{Cl}, t_j^{Cl} and u_j^{Cl} in addition to the parameters defining the internuclear potential energy $V(z)$ according to Eq. (3). We discovered that only ten parameters were required to provide a normalised standard deviation 0.99 and an F-value 5.4×10^{15}; these parameters comprised $U_{1,0}$, $U_{0,1}$, c_j with $1 \leq j \leq 6$, t_0^{Cl} and either u_2^{Cl} or s_0^{Cl} . When we fitted t_0^{Cl} , a value of u_1^{Cl} proved redundant. For the same reason as for SiS above, we hence chose s_0^{Cl} rather than u_2^{Cl} ; resulting values of molecular parameters appear in Table I. The range of validity of these radial functions of AlCl is $1.90 \leq R/10^{-10}\mathrm{m} \leq 2.48$.

Table I
Coefficients of radial functions and other molecular properties of AlCl and SiS, all independent of nuclear mass[a]

Parameter	Values	
	AlCl $X^1\Sigma^+$	SiS $X^1\Sigma^+$
c_0/m^{-1}	23789017.5±205.	46282813.8±91.
c_1	−2.174028±0.000020	−1.9976286±0.0000084
c_2	2.838053±0.00044	1.805768±0.000054
c_3	−2.27475±0.0031	−0.93086±0.00167
c_4	0.3737±0.041	−0.1722±0.0126
c_5	0.430±0.34	1.1348±0.072
c_6	6.517±0.65	−1.011±0.080
s_0^M	[0]	1.754±0.056
s_0^X	−2.723±0.58	−0.311±0.090
t_0^M	[0]	[−1.173]
t_0^X	−1.453±0.036	[−1.547]
$U_{1,0}/\mathrm{m}^{-1}u^{1/2}$	188021.615±0.86	289563.916±0.29
$U_{0,1}/\mathrm{m}^{-1}u$	371.51731±0.00021	452.907106±0.0000129
k_e/Nm^{-1}	208.28888±0.00192	494.01418±0.00103
$R_e/10^{-10}\mathrm{m}$	2.1301429±0.0000019	1.9292731±0.0000016

[a] Each specified uncertainty denotes one estimated standard error propagated from input data of frequencies and wavenumbers; errors of k_e and R_e include uncertainties of fundamental constants h and N_a; brackets enclose values, of which estimated standard errors are discussed in the text, that were constrained during fits of input spectral data. M =Al or Si and X =Cl or S.

4. Discussion

According to only ten independent parameters for AlCl we fitted almost 2300 pure rotational and vibration–rotational transitions essentially within the uncertainties of their measurements. Of these ten parameters all are statistically well defined except c_5 and $s_0^{\rm Cl}$. In the former case the uncertainty is not abnormally large, but the magnitude of c_5 is exceptionally small, such that the ratio $c_5/\delta c_5$ is of order unity; c_5 is certainly required in the final set of parameters because c_6 is evaluated significantly and because by the nature of the truncated polynomial form of $V(z)$ and the nonlinear dependence of $\tilde{E}_{vJ}$ on coefficients c_j, it would be impracticable to include c_6 without also c_5. That the ratio of the magnitude of $s_0^{\rm Cl}$ to its uncertainty is about five assures its significance, although $t_0^{\rm Cl}$, the other parameter to absorb the deviations from mass scaling according to the reduced mass that arise from extra-mechanical effects, is much better defined. According to Eqs (10) and (11), the significant magnitude of $t_0^{\rm Cl}$ implies a similarly significant magnitude of $t_0^{\rm Al}$ that we estimate to be -1.16 ± 0.06; the uncertainty of this estimate and also that of $g_J = -0.084 \pm 0.008$ of ^{27}Al^{35}Cl that we predict reflects the poorly estimated electric dipolar moment of AlCl, $(5 \pm 1.7) \times 10^{-30}$ Cm [21]. This value of the rotational g factor roughly comparable with values of g_J of only few related species, for instance ^{205}Tl^{35}Cl of which $g_J = -0.028058$ [22], for group 13 fluorides [23] with g_J in the range $[-0.08, -0.05]$ and specifically -0.0805 for ^{27}Al^{19}F [24]. For the latter fluorides $t_0^{\rm F}$ is about -1.0 ± 0.02 independent of the metallic atomic partner [23], whereas for TlCl $t_0^{\rm Cl} = -0.94239$, from g_J and μ_e [22]; the latter values are roughly comparable to our deduction $t_0^{\rm Cl} = -1.453$ in AlCl and $t_0^{\rm s} = -1.547$ in SiS.

The major advance in our analysis is the fitting of parameters related directly to the nonadiabatic vibrational effects. As explained above, to derive values of $s_0^{\rm Si}$, $s_0^{\rm S}$ and $s_0^{\rm Cl}$ we relied on the assumption that adiabatic effects are small by comparison with these nonadiabatic vibrational effects, but evidence that u_1 of any atomic centre adopts an undefinably small magnitude when t_0 is constrained or fitted strongly justifies such an assumption. These two molecules AlCl and SiS are the first two examples of such a fitting scheme; other instances of moderately massive nuclei, i.e. more massive than H or Li but less massive than In or Tl, must be expected to follow the present examples. In this way our present analyses of spectra of AlCl and SiS have progressed since our previous analysis of SiS [7] to a more meaningful quasiphysical interpretation. We describe this advisedly as quasiphysical because, although these nonadiabatic and adiabatic effects are primarily artifacts of separate treatment of electronic and nuclear motions, in their representations as polynomials in z according to Eqs (4)–(6) they have almost as firm a physical basis in classical concepts as the potential-energy function, Eq. (3). For $R \sim R_e$ of either molecule the last term in Eq. (9) contributes only about one per cent to the total value of g_J; hence for both AlCl and SiS most contribution to g_J is genuinely a nonadiabatic rotational effect, meaning related to the electrons imperfectly following the nuclei during molecular rotation, or more formally interactions between the electronic ground state and electronically excited states of class $^1\Pi$.

Comparisons with other treatments of these sets of spectral data are appropriate. In their original treatment of the same data of AlCl, Hedderich et al [6] employed for potential energy instead of our $V(z)$ an exponential function of form $\{1 - \exp[-\Sigma\beta_j(\frac{1}{2}z)^j]\}^2$ in which the argument is $\frac{1}{2}z$ according to our definition in Eq. (2); coefficients β_j are fitting parameters. Of the seven parameters required to define the potential energy, five are of type β_j, $0 \le j \le 4$; another two are R_e

and D_e analogous to the equilibrium binding energy of the Morse function. The value of D_e, constrained from thermochemical data of accuracy about one per cent, can obviously influence values of other, fitted parameters far beyond their nominal precision as great as one part per million. Apart from no account being taken of the rotational g factor, which is known [16] to affect significantly the value of R_e (if sought to be independent of mass), the stated uncertainty attached to the value $(2.130143506503515 \pm 5.21 \times 10^{-8}) \times 10^{-10}$ m is unrealistically small, even without account being taken of experimental uncertainties of constants h and N_A that enter the calculation. Because of this omission of the effect of g_J, the fact that their value of R_e is within one standard error of our value is fortuitous. In agreement with our eight values of parameters to define the internuclear parameter (R_e, c_j, $0 \leq j \leq 6$, or equivalent), Hedderich et al required eight values of the corresponding parameters R_e and coefficients a_j according to Dunham's definition; despite the fact that their Eq. (17) is incorrect, their value of a_0 appears unaffected. Even though their selected functional form provides in a simple way a qualitatively acceptable approach to the dissociation limit as $R \rightarrow \infty$ or $\frac{1}{2}z \rightarrow 1$, the exponential form is quantitatively incompatible with the correct form, namely an inverse dependence on R (specifically, R^{-6}), unlike the polynomial in z, Eq. (3), that can be extended to bestow the quantitatively correct form [13].

To encompass extra-mechanical effects in their "parametrized potential mode", Hedderich et al [6] used the displacement variable $(R - R_e)$ as argument of a truncated polynomial and evaluated two coefficients pertaining to the atomic centre Cl. Apart from the facts that this variable is ill behaved as $R \rightarrow \infty$ and that no range of validity of their radial functions was specified, the nature of these terms relative to the effective Hamiltonian in Eq. (1) corresponds to $V'(R)$, thus to adiabatic effects. We demonstrate here that such adiabatic effects appear negligible for SiS and AlCl, and have instead evaluated variables related to nonadiabatic rotational and vibrational effects. Although parameters of their model may enable satisfactory reproduction of spectral data — the frequencies and wavenumbers of transitions, not only are they devoid of physical meaning, but also they imply an incorrect nature of the quasiphysical effects. Without extensive numerical calculations involving innumerable integrations of Schroedinger's equation, proof of reproducibility of the original spectral data is impossible; even if presented values of parameters a_j were used with Dunham's relations for the potential energy, corresponding to simple relations connecting c_j to Y_{kl} in Eq. (7) [11], the absence of corresponding analytic relations to relate the coefficients of $(R - R_e)$ to the additional term coefficients Z_{kl} of any type means that these values of a_j corresponding to any model - constrained or unconstrained Dunham, or parametrized potential - are useless for the purpose of reproducing the spectral data from which they were deduced. In contrast, our generation of Y_{kl} and all required Z_{kl} according to simple analytic relations published [11] also available in machine-readable form [25], is a trivial computing task, readily achieved with even a modest programmable calculator. From our fitted value of t_0^{Cl} we succeeded to predict a value of parameter g_J for AlCl related to a genuinely physical measurement, the Zeeman effect on pure rotational transitions for instance, whereas their coefficients of $(R - R_e)$ imply no such meaning whatsoever. As our programme Radiatom generates also values of $\Delta_{kl}^{a,b}$ according to Eq. (8), we compare our values $\Delta_{1,0}^{\mathrm{Cl}} = -1.36 \pm 0.15$ with -1.29 ± 0.14 (unconstrained) or -1.223 ± 0.095 (constrained) [6] and $\Delta_{0,1}^{\mathrm{Cl}} = -1.453 \pm 0.036$ with -1.443 ± 0.029 (unconstrained or constrained) [6]. The agreement is satisfactory, but unconstrained values of U_{kl} lack justification [26, 27].

Following our previous analysis of spectral data of SiS [7], an alternative analysis of the same data was reported [28]. The authors claimed that their work purports to be a direct determination of analytic diatomic potential-energy functions from spectral data; because a potential-energy function is not an observable quantity such a determination is logically impossible. In any case the process of deriving these functions is not direct but an inversion that has never been proved unique [29]. The maximum physical meaning accrues from these and auxiliary functions if the rotational g factor is taken into account. Appearing in Table I, our values of $t_0^{\mathrm{Si,S}}$, which we constrained during the fits of the spectral data, were so derived by means of Eqs (10) and (11); not there specified are the associated uncertainties, 0.015 in each case, that propagated from the known standard errors of g_J [10] and μ_e [9]. These data were ignored in the other analysis [28] in which four or five parameters pertaining only to adiabatic effects were incorporated.

One problem that evidently arises in fits according to this numerical approach [28] is equivalent to an inability to distribute the vibration–rotational terms $\tilde{E}_{vJ}$ correctly among the various term coefficients Y_{kl} and Z_{kl} in Eq. (7). Although Frum et al demonstrated conclusively significant evaluation of both $U_{4,0}$ and $Y_{4,0}$ of $^{28}\mathrm{Si}^{32}\mathrm{S}$ [30], which imply directly a significant value of a_6, or equivalent c_6 in Eq. (3), Coxon and Hajigeorgiou [28] evaluated potential-energy coefficients until only c_5 or their β_5 and absorbed instead the extra required effect of the potential energy into their coefficient u_3^{Si}; the equivalent parameter h_3^{Si} was, however, determined in neither their work [28] nor our previous results [7]. To ascertain unambiguously whether the coefficient c_6 (or an equivalent parameter for potential energy) is required, we fitted the data of the frequencies of the pure rotational transitions and the wavenumbers of the vibration–rotational transitions of only the most abundant isotopic variant $^{28}\mathrm{Si}^{32}\mathrm{S}$, for which data are reported up to $v = 10$ [30]. Under these conditions the effective potential energy becomes the adiabatic potential energy in that the adiabatic vibrational effects and part of the nonadiabatic vibrational effects are necessarily absorbed into the evaluated coefficients for the potential energy; obviously no parameters to take into account the separate dependence of the vibration–rotational terms on the mass of either nucleus are determinable because within a single isotopic variant no variation of these masses is practicable. By comparison with the fit of 1723 spectral lines with only seven varied parameters (k_e, R_e and $c_1 - c_5$), the inclusion of c_6 yielded a normalised standard deviation significantly decreased by eight per cent and — even more instructively — an increased F value. The deduced value of c_6 was -3.3 ± 0.9, hence significant, and the largest associated correlation coefficient, of magnitude 0.91, connected c_6 with c_4. Moreover, when a variable was introduced to take into account any rotational effects additional to those related to the adiabatic potential energy, a significant value $g_1' = 0.074 \pm 0.033$ resulted, and the maximum magnitude of any correlation coefficient connecting this variable to any other was only 0.20. By the nature of its occurrence in the equations for Z_{kl} [8], $-g_1'$ is associated roughly with the rotational g factor; indeed this value of $-g_1'$ is remarkably similar to $g_J = -0.090974 \pm 0.000065$ determined directly from the Zeeman effect [10], even though the former value resulted from measurements of only one isotopic species in the absence of externally applied electric or magnetic field. Despite the marginal significance of the value 0.074, as the magnitude is about twice its standard error, this result is further confirmation that the additional rotational effects represented by the coefficients Z_{kl}^r (for both nuclei concurrently through the reduced mass) can be determined separately from those due to the vibration–rotational effects represented by Z_{kl}^v. For this reason the term coefficients Y_{kl} should be regarded not as independent fitting parameters but be constrained by means of the known inter-relations [25]. Because of our explicit use of the experimental rotational g factor [10] to constrain values of $t_0^{\mathrm{Si,S}}$, we deduced an improved value, truly independent of mass, of the equilibrium internuclear distance R_e; given in the Table, this value is distinct from that generated in previous treatments [7, 28], between which there was satisfactory agreement. Hedderich et al proved that the exponential form of the potential-energy function used by Coxon and Hajigeorgiou [28] exhibits nonphysical behaviour at large R despite the intent of its exponential form being to display a qualitatively correct approach to the dissociation limit.

Further comparisons between the conduct of our approach and that of Coxon and Hajigeorgiou [28] are pertinent. We fit the measured spectral data (frequencies and wavenumbers of assigned transitions) to analytic expressions directly generated by entirely quantum-mechanical means [8], whereas their approach is entirely numeric; that their approach is unreliable for a comparable molecular species CO is conclusively demonstrated [31], and further proof of its deficiencies in application to the hydride LiH [32] will be described elsewhere. According to both analytic and numeric approaches, however, as the parameters of the radial functions to be evaluated are related nonlinearly to the observable data, one uses an iterative — hence indirect — computational method starting with initial estimates of parameters, rather than a direct method that would be applicable if the dependences of the observable quantities on the parameters were linear, as in Eq. (8). Hence for this further reason the claim of Coxon and Hajigeorgiou [28] of direct determination of an analytic potential-energy function of SiS or other molecules is fallacious. These authors stated that they achieved convergence normally after two iterations, each of which for SiS required about 30 minutes on a microcomputer (80486 processor at 33 MHz), from "a reasonably good set of trial parameters". Our programme requires typically about 13 iterations for hydrides or ten iterations for nonhydrides, such as SiS, and is designed to probe comprehensively the parameter space to find the optimum solution; for this reason the final converged values of the parameters, and even the number of iterations, are insensitive to the initial values. Indeed initial values of most unconstrained parameters, except rough values of $U_{1,0}$, $U_{0,1}$ and $c_1 - c_3$, are customarily set to zero; tests with alternative initial values, widely varied, have never yielded final estimates of the parameters distinct from those based on zero initial values. Despite the more numerous iterations, our programme requires for these 3025 data of SiS only about one hour of total cpu time for compilation and execution on a DEC VAX 8530 machine (using in Fortran 77 code the representation REAL*16 of real numbers that enables about 32 decimal digits to be carried throughout the computations so as to ensure maximum numerical significance of the results); the speed of this machine for Fortran in REAL*8 precision is comparable with that of a superior microcomputer (80486 processor at 25 MHz). Thus our algorithm and its implementation are computationally more efficient, in terms of duration, and more reliable, because of both the greater numerical precision (which is important when the input data contain nine or more significant decimal digits in the most precise cases) and the greater area sampled on the parameter hypersurfaces, than the numerical method and programmes that Coxon and Hajigeorgiou [28] have applied to essentially the same spectral data of SiS.

5. Conclusion

We have demonstrated how numerous spectral data, namely the frequencies and wavenumbers of pure rotational and vibration–rotational transitions, of both AlCl and SiS are reproduced accurately by means of physically meaningful parameters in a small set. In general one cannot distinguish among all three extra-mechanical effects due to finite nuclear mass on the basis of only variation of isotopic mass and the additional rotational effects. On the basis of a reasonable and justified assumption that the adiabatic effects are relatively small, we have, however, discovered information about both nonadiabatic rotational and nonadiabatic vibrational effects in both AlCl and SiS from their spectra. Furthermore, we have shown how we can predict physically determinable parameters, specifically g_J, by means of this analytic and computationally efficient approach that incorporates distinct advantages relative to purely numeric approaches.

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